RESTRICTED ROTATION IN SOME ARYL AMINES

BY

JOSEPH GORDON

B.A., Amherst College, 1945

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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R. UNIV. BIBLIOTHEEK LEIDEN

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Introduction

Optical isomerism due to restricted rotation around the carbon-nitrogen bond has been studied in several aromatic amines. N-Succinyl-N-methyl-3-bromomesidine (I) was resolved into its active form, and its half-life period was determined (1). A series of N-succinyl-1-methylamino-2,4-dimethyl-6-substituted benzenes were also resolved into their active forms and their half-life periods determined (2). The substituents included bromo (II), iodo, nitro, and amino groups. The results indicated relative optical stabilities which were in disagreement with those found in analogous compounds in the biphenyl series and contrary to what would be expected from space considerations only. It was suggested that these electronegative substituents lowered the basicity of the amine, and that this basicity was a major factor in the optical stability of the compound. Evidence of this theory came when N-succinyl-1-methylamino-2-methyl-4,6-dibromobenzene was resolved. It had a half-life approximately one-third that of the monobromo compound (II).

Discussion Of Results

N-Succinyl-1-methylamino-2,4-dimethyl-6-chlorobenzene was prepared, resolved into its active forms and its half-life determined to be thirty-three minutes in boiling *n*-butanol and approximately sixty-three hours in boiling methyl acetate. Compound II had a half-life of 3.2 hours in boiling butanol. N-Succinyl-1-methylamino-2-methyl-4,6-dichlorobenzene was prepared and resolved into its active forms. It was completely racemized in thirty minutes in boiling butanol but had a half-life of about eighteen hours in boiling methyl acetate. The second chlorine could affect the stability only through its change in the basicity of the amine. The decrease in stability of chlorine over bromine is greater than would be anticipated from size considerations only. Basicity of the amine, there-

fore, must be an important factor in the optical stability of these compounds.

N-Benzenesulfonyl-N-carboxymethyl-1-amino-3-bromomesidine was prepared and resolved into its active forms. It had a half-life of eight hours in boiling butanol, which is to be compared with a half-life of nine hours for (I). It appears that the N-benzenesulfonyl-N-carboxymethyl grouping offers less hindrance than the N-succinyl-N-methyl grouping. This might be due to the acid nature of the sulfonamide group.

N-Benzenesulfonyl-N-carboxymethyl-1-amino-2,4-dimethyl-6-bromobenzene (III) and N-benzenesulfonyl-N-carboxymethyl-2,4-dimethyl-6-nitrobenzene (IV) were prepared by Yuan (3) but could not be resolved. These compounds have now been resolved. Compound III was resolved through its cinchonidine salt which was decomposed to give both active forms. Its half-life in boiling butanol was 2.5 hours. Compound IV formed a mutarotating salt with cinchonine which had a half-life of thirty-two hours at 31°. The active form prepared from this salt gave an optically unstable compound which had a half-life of 2.25 hours in boiling methyl acetate.

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VITA

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